

# PATENT SPECIFICATION

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## (54) RECOVERY OF FLUORINE AND PHOSPHATE VALUES FROM WASTE WATER

(71) We, OCCIDENTAL PETROLEUM CORPORATION, a Corporation organised and existing under the laws of the State of California, United States of America, of 10889 Wilshire Boulevard, Los Angeles, California 90024, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with recovering fluorine and phosphate values from the waste waters ("pond waters") resulting from the production of wet process phosphoric acid, having as an objective the recovery of such values in the form of calcium fluoride and calcium orthophosphate while neutralizing the waste waters so they can be discharged into rivers and streams without fear of pollution, or be recycled as process waters in the production of phosphoric acid.

A wet process phosphoric acid plant using the dihydrate technique uses large amounts of water, typically at a rate of about 50 gallons per minute for each unit of plant output capacity as measured in product  $P_2O_5$  tons per day: this is equivalent to about 210 litres per minute per unit of plant output capacity expressed in tonnes per day. Much of this water is repeatedly recycled but a substantial amount is continually directed to a waste pond to restrict accumulation of contaminants in the water. The pond water contains from about 0.1 to about 5% fluorine, from about 0.1 to about 5%  $P_2O_5$ , from about 0.1 to about 2.5%  $SiO_2$ , from about 0.1 to about 0.5% dissolved calcium and from about 0.1 to about 0.5% soluble sulphate salts (unless otherwise indicated, all percentages herein are weight percentages). The fluorine content of such pond water is of major concern because it can present an ecological hazard, while the  $P_2O_5$  content both represents a loss of a valuable product and an ecological hazard.

Traditionally pond waters have been passed through settling basins prior to their discharge into rivers and streams. At times, pond waters are treated with limestone and lime to pre-

cipitate out fluorine and other values before discharge to meet pollution control laws and regulations. In the settling basins, the amounts of the various chemical values, such as fluorine,  $P_2O_5$ , calcium, etc., in the water decrease so that the pond water when discharged into the streams contains lesser, but appreciable, amounts of these materials. Not only does this discharge of pond waters add chemical values to streams, but it also causes a decrease in the pH of the streams. Pond water typically is acidic and has a pH from about 1 to about 3.

Workers in the art have recognized the economic loss and ecological problem of pond waters and have developed methods of treating pond waters. However, it appears that none of these methods have been economically attractive or feasible since none of the methods are in commercial use in the United States. For example, D. R. Randolph developed a method which is disclosed in U.S. Patent 3,625,648. The Randolph method comprises treating pond water with milk of lime to adjust the pH of the resulting slurry to between about 3.2 and 3.5 whereby 99% of the available fluorine is precipitated out as calcium fluoride. The calcium fluoride is separated from the aqueous phase and treated with sulphuric acid, or other strong acid, to liberate the hydrogen fluoride (HF) gas and yield a slurry of gypsum, sulphuric acid and phosphoric acid. The latter slurry can be recycled back into a conventional wet acid phosphoric acid process to recover the  $P_2O_5$  values. The HF gas can be upgraded by conventional methods. The aqueous phase, after removal of the calcium fluoride, is treated with an additional 10% milk of lime to adjust the pH to between 4.7 and 5 to precipitate out dicalcium phosphate. Dicalcium phosphate is separated from the aqueous phase and is upgraded in a conventional dicalcium phosphate plant or cycled to a conventional wet process phosphoric acid plant to recover the phosphate values. The aqueous slurry is then treated with additional milk of lime to adjust the pH to between 6 and 7 wherein further solids precipitate out, such

as gypsum. The solids are separated from the now almost neutral aqueous phase and passed to waste. The aqueous phase is then recycled as process water to the phosphoric acid plant or discharged into streams or rivers.

The object of the present invention is to provide an economic method of treating phosphate waste waters so as to recover many of the valuable chemical values therein which are ecologically undesirable products in streams and lakes. The present invention also aims to provide a method of rendering the pond waters neutral so that they can be discharged into streams or rivers or recycled as process water.

The present invention thus provides a method of treating waste water resulting from the production of wet process phosphoric acid and containing fluorine and  $P_2O_5$  values, comprising: in a first stage, agitating said waste water with an amount of calcium carbonate to provide between 0.3 and 0.8 equivalents of calcium per equivalent of fluorine (F) values in the water; thereafter, in a second stage, agitating the calcium carbonate-treated waste water with additional calcium carbonate in an amount to form calcium fluoride solids, and such that the total calcium carbonate addition in the two stages provides not less than 0.8 equivalents of calcium per equivalent of F values in the waste water; and separating the solids from the aqueous phase following said second stage.

In typical practice of the method, the waste or pond water is treated with calcium carbonate in the form of ground limestone or in the form of an aqueous slurry of ground limestone. In the first stage, this calcium carbonate addition results in the formation of calcium salts containing phosphate and fluorine values. Preferably about 0.4 equivalents of calcium per equivalent of fluorine in the pond water is added in the first stage, which is normally carried out at the temperature of the pond water but which may, however, be carried out at any temperature between the freezing temperature of the pond water and its boiling point. The residence time for this first stage is usually one-half minute to 60 minutes, being preferably about 5 minutes. The pond water and the calcium carbonate are agitated to ensure maximum reaction between the calcium carbonate and the pond water values.

The treated pond water is then passed to a second stage wherein additional calcium carbonate is added so that the total addition of calcium carbonate in the two stages is not less than 0.8 equivalents of calcium per equivalent of fluorine initially present in the pond water, the second stage addition preferably being such as to result in a total addition of 1 to 2 equivalents of calcium per equivalent of fluorine. The second stage treatment is also normally carried out at the pond water temperature although, like the first stage treat-

ment, the second stage treatment may be carried out at any temperature between the freezing point of the treated pond water and its boiling point. The residence time in the second stage is usually from one-half minute to 60 minutes, being preferably about 30 minutes.

In the second stage a slurry is formed containing solid calcium fluoride and some solid calcium phosphate values. This slurry is passed to a separation stage wherein the solids are separated from the aqueous phase. The resulting solid cake is preferably washed in an acid wash stage with an aqueous solution of a strong mineral acid, such as sulphuric acid, to remove phosphate and other values from the solid calcium fluoride phase thereby to raise the F/ $P_2O_5$  weight ratio thereof. Preferably the solids are washed with an amount of mineral acid about equivalent to the total of the  $P_2O_5$  and  $CO_2$  values contained in the solids. The solid phase is subsequently washed with water in a water wash stage to substantially remove most of the aqueous soluble values and mineral acid, leaving a solid product that may contain up to about 45% by weight fluorine as calcium fluoride.

The aqueous mineral acid washings and the wash water from the solids are preferably combined with the treated waste water effluent of the second stage in a mixer wherein they are mixed together to form a first stream which is passed to a third stage wherein it is agitated with calcium oxide, such as ground lime or aqueous lime slurry, in an amount sufficient to raise the pH of the first stream to a value ranging from 3 to 4, preferably between 3.6 and 3.8, the pH of the first stream usually being initially between 1.8 and 2.6 because of the addition of wash acid. In this third stage, a substantial proportion of the remaining fluorine values in the aqueous mixture is converted to additional calcium fluoride which is conveniently separated from the stream in a separate stage to yield a second crop of calcium fluoride solids which is recycled to the acid wash stage where it is subjected again to the acid washing and water washing to produce solids enriched in calcium fluoride. This second crop of solids can be combined with the solids separated from the second stage effluent.

The aqueous phase from the said separator stage is conveniently passed as a second stream to a fourth stage wherein it is treated with further calcium oxide to raise the pH of the aqueous mixture to a value ranging from 5 to 8, preferably from 6.5 to 7.2. In this fourth stage, calcium orthophosphate ("dical" or dicalcium phosphate) precipitates out and is subsequently separated from the stream in a second separator stage to yield "dical" solid. The aqueous phase from the second separator stage may then be passed as a third stream to a fifth treatment stage

wherein the third stream is further treated with calcium oxide to raise the pH of the aqueous mixture to a value ranging from 8 to 11 to remove a substantial proportion of the soluble mineral values of the aqueous mixture by formation of insoluble mineral solids. The calcium oxide is normally added to the third, fourth and fifth stages in the form of an aqueous slurry having a solids content of 5 to 50%, preferably from 10 to 25%. The calcium oxide slurry is prepared from fresh water, not pond waters or process waters containing F and  $P_2O_5$  values. The mixture from the fifth stage is passed through a third separator stage wherein solids, mainly calcium values and silicon dioxide, are separated from the aqueous phase and passed to waste. The remaining aqueous phase is water which is substantially free of fluorine,  $P_2O_5$ , calcium and  $SiO_2$  values and can be recycled back into a wet process phosphoric acid plant.

The accompanying drawing is a schematic illustration of an embodiment of the method of the present invention.

Referring to the drawing, pond water is passed to the first reactor stage 10. Simultaneously, a stream of slurried calcium carbonate 12 is also passed to the reactor 10. The stream 12 originates in a mixer 14 wherein a source of ground calcium carbonate, such as limestone, is mixed with fresh water, not pond water or process water containing F or  $P_2O_5$  values, to form the calcium carbonate slurry. The calcium carbonate source is ground to at least -10 mesh (U.S. Standard), preferably to 90% -200 mesh. The calcium carbonate slurry is formulated with a solids content of between 5 and 50%, preferably 10 to 25%. The calcium carbonate slurry and pond water are agitated in the reactor for about 5 minutes, although shorter or longer reaction time can be employed. The amount of pressed as equivalents of calcium added to calcium carbonate added to reactor 10, expressed as equivalents of calcium added to the pond water per equivalent of fluorine in the pond water, is designated  $Z_1$  and has a value ranging from 0.3 to 0.8, preferably having a value of about 0.4. The reaction that occurs in reactor 10 normally produces soluble calcium values such as  $CaSiF_6$ , although in some instances insoluble values will be formed. Preferably the reaction is so managed that no solids will be formed in reactor 10.

The reaction mixture from reactor 10 is passed as a stream 16 to a second reactor stage 18 wherein the stream 16 is mixed with additional slurried calcium carbonate via stream 20. The stream 20 also originates from the mixer 14.

The reaction mixture in reactor 18 is agitated for a period of about 30 minutes, although shorter or longer residence times as described above can be employed. The amount of calcium carbonate added to reactor 18, expressed as equivalents of calcium per equivalent of fluorine in the pond water, is designated as  $Z_2$ .  $Z_2$  is equal to at least  $Z_R$  minus  $Z_1$ , where  $Z_R$  designates the minimum amount, in stoichiometric equivalents, of calcium that can be added to reactors 10 and 18 to remove from 85 to 100% of the fluorine values from the feed pond water.  $Z_R$ , on a mineral acid-free basis, has a value equal to  $1+0.19 R_w$ , where  $R_w$  is the weight ratio of  $P_2O_5$  to fluorine in the pond water.  $Z_R$  usually has a value of from 1 to 2.  $Z_2$  has a value ranging from 0.1 to 2, preferably being from 0.4 to 1.4; and an especially preferred range of  $Z_2$  values is from 1 to 1.4. In theory, the  $Z_R$  value should provide sufficient calcium to remove substantially all the fluorine from the pond water. However, as explained above, the pond water contains other values besides fluorine, such as  $P_2O_5$  and sulphate, which can complex with the calcium and limit the amount of calcium available for reaction with the fluorine values. The  $Z_R$  value takes account of those other values. Preferably more calcium is added, such as 5% excess, than calculated from the  $Z_R$  value. However, excessive amounts of calcium are not necessary and interfere with the acid wash stage described below.

The reaction mixture from reactor 18 is passed as a stream 24 to a first separator stage 26. At least 85% of the fluorine values in stream 24 are solid calcium fluoride, preferably at least 95% of the fluorine values being solid calcium fluoride. In addition, substantially all the iron and aluminium values in the stream 24 are present as solids, and about 50% of the sulphate values and 25 to 50% of the  $P_2O_5$  values are present as solids.

The separator 26 is a conventional liquid-solid separator, such as a filter, a centrifuge or a decanting tank. The calcium fluoride solids are separated from the liquid phase of stream 24 in separator 26 and passed as a stream 28 to an acid washer 30. The solids are washed with a stream 31 of an aqueous solution of a strong mineral acid in the washer 30, the solids being washed with a 1% to 50% (w/w) mineral acid solution, preferably a 5% to 25% (w/w) acid solution. The calcium fluoride solids are preferably washed with an amount of mineral acid about equivalent to the  $P_2O_5$  and  $CO_2$  values contained in the solids, plus or minus 10%. The acid concentration and wash temperature are so controlled that reaction between the fluoride values and the acid is minimized to prevent formation of hydrogen fluoride. The maximum wash temperature is about 180°F (82°C). Although any strong mineral acid, such as hydrochloric, perchloric, nitric, sulphuric, hydrofluoric or other strong mineral acid, can be used in the wash step, sulphuric acid is preferred. In this acid wash step, a substantial portion of the  $P_2O_5$  values are removed from the solid product. In addition,

The reaction mixture from reactor 10 is passed as a stream 16 to a second reactor stage 18 wherein the stream 16 is mixed with additional slurried calcium carbonate via stream 20. The stream 20 also originates from the mixer 14.

The reaction mixture in reactor 18 is agitated for a period of about 30 minutes, although shorter or longer residence times as described above can be employed. The amount of calcium carbonate added to reactor 18, expressed as equivalents of calcium per equivalent of fluorine in the pond water, is designated as  $Z_2$ .  $Z_2$  is equal to at least  $Z_R$  minus  $Z_1$ , where  $Z_R$  designates the minimum amount, in stoichiometric equivalents, of calcium that can be added to reactors 10 and 18 to remove from 85 to 100% of the fluorine values from the feed pond water.  $Z_R$ , on a mineral acid-free basis, has a value equal to  $1+0.19 R_w$ , where  $R_w$  is the weight ratio of  $P_2O_5$  to fluorine in the pond water.  $Z_R$  usually has a value of from 1 to 2.  $Z_2$  has a value ranging from 0.1 to 2, preferably being from 0.4 to 1.4; and an especially preferred range of  $Z_2$  values is from 1 to 1.4. In theory, the  $Z_R$  value should provide sufficient calcium to remove substantially all the fluorine from the pond water. However, as explained above, the pond water contains other values besides fluorine, such as  $P_2O_5$  and sulphate, which can complex with the calcium and limit the amount of calcium available for reaction with the fluorine values. The  $Z_R$  value takes account of those other values. Preferably more calcium is added, such as 5% excess, than calculated from the  $Z_R$  value. However, excessive amounts of calcium are not necessary and interfere with the acid wash stage described below.



other values, such as  $\text{CaCO}_3$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , are also removed from the solid in varying amounts by the acid wash.

5 The washed slurry stream 32 leaving the washer 30 is passed to separator 34 wherein the solids are separated from the aqueous phase. Separator 34 is a conventional liquid-solid separator. The solids from separator 34 are passed as stream 36 to a water washer 38  
10 wherein the solids are washed with fresh water, not process waters or pond waters. The solids are washed with at least an equal weight amount of water, preferably about 2 weights of water, although larger amounts of water can be used in the wash. The water wash removes many of the soluble  $\text{P}_2\text{O}_5$  values from the solids.

20 The acid wash and water wash up-grade the calcium fluoride solids with respect to the percentage of contained fluorine and the  $\text{F}/\text{P}_2\text{O}_5$  weight ratio.

25 The washed solids product of the washer 38, as a slurry, is passed to a third separator stage 42 as a stream 44. Separator 42 is a conventional liquid-solid separator such as the separator 26 described above. Solids are separated from stream 44 in separator 42 to yield a cake containing up to about 45% fluorine as calcium fluoride. The cake can be processed by conventional means (not shown) into hydrogen fluoride or it can be dried by conventional means (not shown), e.g. at a temperature between 90 and 150°C, and stored or transported as a dry solid. The calcium fluoride cake is mostly calcium fluoride; however, the cake could also contain a small amount of  $\text{P}_2\text{O}_5$  values (usually less than about 5%), silicon dioxide values (usually less than about 3%) and sulphate values.

40 Thus the calcium fluoride solids of the cake are normally of sufficient purity to prepare hydrogen fluoride directly therefrom by heating the cake solids with sulphuric acid by conventional methods. If the  $\text{P}_2\text{O}_5$  concentration is greater than about 5 to 10% or if the silicon dioxide concentration is greater than 5% in the cake solids, it is difficult to prepare good quality hydrogen fluoride from the calcium fluoride solids by treatment with sulphuric acid, since at high temperature in an acid environment, phosphorus and silicon will react with fluorine to produce gaseous fluorine values such as  $\text{PF}_3\text{O}$ , and  $\text{SiF}_4$ , which contaminate the hydrogen fluoride produced and are difficult to remove. Accordingly, it is one of the achievements of the present invention that a calcium fluoride solid product can be obtained which can be directly converted into hydrogen fluoride by conventional means.

60 The aqueous phases from the separator 26, 34 and 42 are passed to a mixer 48 as streams 50, 52 and 54 respectively. In the mixer 48, the various streams are thoroughly mixed together and passed to a third reactor stage

56 as stream 58. In the mixer 48 some solids, mainly gypsum, may settle out and are removed as stream 60 as waste solids.

In reactor 56, stream 58 is reacted with a slurry of calcium oxide from stream 62. 70 The origin of stream 62 is a mixer 64 wherein a ground calcium oxide feed source, such as lime, and water are mixed to form a calcium oxide slurry. The calcium oxide feed source is ground to at least -10 mesh (U.S. Standard), preferably at least 90% -200 mesh. 75 The calcium oxide slurry prepared in the mixer 64 contains from 5 to 50% solids, preferably from 10 to 25% solids. The calcium oxide slurry is prepared from fresh water and not pond waters or process waters. 80

The stream 58 has a pH between 1.8 and 2.6. Sufficient slurried calcium oxide is added to reactor 56 to raise the pH of the resulting reaction mixture to a value ranging from 3 to 4, preferably from 3.6 to 3.8. The retention time of stream 58 in reactor 56 is from 30 seconds to 60 minutes, preferably being about 15 minutes. The reaction temperature within reactor 56 may have any value between the freezing and boiling points of the reaction mixture but is preferably about ambient temperature. The reaction mixture contains 0.01 to 0.2% fluorine, a substantial portion of which is precipitated out as calcium fluoride upon the addition of the calcium oxide. 85 90 95

The reaction mixture from the reactor 56 is passed to a fourth separator stage 68 as stream 70. The separator stage 68 is a conventional liquid-solid separator such as the separator 26 described above. The solids separated out in the separator 68 consist of calcium fluoride and phosphate values and are recycled as stream 72 to stream 28 wherein the solids undergo the acid wash and the water wash as described above as part of stream 28. 100 105

The aqueous phase separated in separator 68 is passed to a fourth reactor stage 74 as stream 76. In reactor 74, the aqueous phase is treated with slurried calcium oxide from stream 75 which has its origin from mixer 64. The reaction temperature and reaction residence time in the reactor 74 are similar to those in reactor 56. The pH of the stream 76 is from 3 to 4. Sufficient calcium oxide is added to reactor 74 to raise the pH of the reaction mixture to between 5 and 7 to cause the precipitation of "dical" (calcium orthophosphate or dicalcium phosphate). The reaction slurry from reactor 74 is passed to a fifth separator stage 78 as stream 80. The separator 78 is a conventional liquid-solid separator such as the separator 26 described above. The solids separated in separator 78 consist principally of "dical". The "dical" produced by this method is of sufficient purity to employ in animal feed. That is, the  $\text{P}/\text{F}$  weight ratio in the "dical" is greater than 100. 110 115 120 125 130

The aqueous phase from the separator 78 is passed to a fifth reactor stage 82 as stream 84. Stream 84 is combined with a calcium oxide slurry from stream 86 in the reactor 82. Stream 86 has its origin from mixer 64. Sufficient calcium oxide is added to the reaction mixture in the reactor 82 to raise the pH to a value of between 8 and 11 thereby to cause precipitation of a substantial portion of the remaining soluble minerals as insoluble values, such as silicon dioxide solids and other solids from the reaction mixture.

The reaction mixture in the reactor 82 is passed to a sixth separator stage 88 as stream 90. The separator 88 is a conventional liquid-solid separator such as the separator 26 as described above. Separated solids from the separator 88, consisting chiefly of silicon dioxide solids, are sent to waste as stream 92.

The aqueous phase from separator 88 consists of a non-acidic water which is substantially free of calcium, fluorine,  $P_2O_5$  and sulphate values. This water is discharged as stream 94 and can be used as a fresh water for industry or it can be discharged into streams or lakes.

In another embodiment of the present invention, ammonia is added to the reaction stream before the stream 80, preferably as the indicated stream 8 to the reactor 18 or to the reactor 10. The ammonia is maintained at a concentration between 10 and 5000 parts per million by weight, preferably a concentration of 600 to 800 parts per million ammonia in the reaction stream. The presence of ammonia in the reaction stream optimizes the yield of calcium fluoride and the P/F ratio of the "dical" produced in reactor 74. The reason for this is not thoroughly understood. However, it is believed that the ammonia complexes with the fluorine values, furnishing soluble fluorine values that can readily react with soluble calcium values to form the insoluble calcium fluoride. Thus the presence of ammonia not only enhances the quality of the produced "dical" but also increases the removal of fluorine from the pond waters and the overall yield of calcium fluoride.

The following Examples illustrate the present invention and compare it with procedures that do not embody it. In these examples, all percentages are weight percentages.

#### EXAMPLE 1

To 3834 grams of pond water containing on a weight basis 0.94% F (predominantly  $H_2SiF_6$ ), 1.70%  $P_2O_5$ , 0.41%  $SO_3$ , 0.59%  $SiO_2$  and other soluble metallic compounds, at 110°F (43°C), were added 34.4 grams of ground commercial limestone (95% effective  $CaCO_3$ ) as a 44.7% aqueous slurry ( $Z_1=0.34$ ). The mixture was agitated for five minutes while pH increased from 1.39 to

1.85. No fluoride values precipitated. Ground commercial limestone (106.9 grams) wetted with water was added to the reaction mixture and agitated ( $Z_2=1.07$ ). 65

$$\begin{aligned} Z_R (\text{theory}) &= 1 + 0.19 \times 1.70 / 0.94 = 1.34; \\ Ca^{++} (\text{used}) &= Z_1 + Z_2 = 0.34 + 1.07 = 1.41\% \\ Ca^{++} (\text{used}) &= 105\% Z_R (\text{theory}) Ca^{++} \end{aligned} \quad 70$$

The pH of the reaction mixture after 37 minutes of agitation was 3.0. Calcium fluoride precipitated from the mixture and was separated therefrom by decantation and filtration, and dried at 105°C. About 141 grams of calcium fluoride solids were recovered having the following analysis: 25.0% F, 15.3%  $P_2O_5$ , 3.6%  $SO_3$ , 49.8%  $CaO$ , <2.0%  $SiO_2$ , <2.0%  $CO_2$  plus other metallics and 12.8% hydration water. The filtrate contained 0.017% F, 1.18%  $P_2O_5$  and 0.62%  $SiO_2$ . The dried calcium fluoride solids were washed with 10%  $H_2SO_4$  and water to reduce the  $P_2O_5$  content of the solids to about 3.5%. The fluorine content of these solids represented about 97.8% of the fluorine in the original pond water. 75 80 85

#### EXAMPLE 2 (Comparative)

To 2000 grams of pond water at room temperature containing 0.84% F and 1.52%  $P_2O_5$ , was added 15.7 grams of ground commercial limestone slurried with water to a solids content of 33% ( $Z_1=0.34$ ). The resulting mixture was agitated for about 5 minutes. Additional ground commercial limestone (17.9 grams) was added to the reaction mixture and the resulting mixture was agitated for an additional 200 minutes to ensure equilibrium conditions ( $Z_2=0.38$ ;  $Z_R=1.35$ ). The mixture was filtered. The filtrate contained 0.64% F and 1.30%  $P_2O_5$ , representing only a 24% fluoride precipitation as calcium fluoride. 90 95 100

#### EXAMPLE 3 (Comparative)

In an experiment similar to that discussed in Example 1, the limestone was totally added at the start of the reaction rather than in two increments. The filtrate still contained about 25% of the fluoride following filtration after 60 minutes of agitation. 105 110

#### EXAMPLE 4

Pond water similar to that used in the previous Examples was heated to 200°F (93°C); and to this solution, 1.4 equivalents of limestone (as a 33% solids slurry) per equivalent of contained fluoride were added in two stages ( $Z_1=0.34$ ) with agitation to precipitate over 85% of the fluorine values as calcium fluoride. No adverse effects due to the temperature were observed. 115 120

#### EXAMPLE 5

Pond water, at room temperature, was diluted ten-fold with water to contain 0.087%

F and 0.153%  $P_2O_5$ . A quantity of pure limestone (as a 35% solids slurry) equivalent to a 129% stoichiometric amount based on initial total fluoride was added incrementally as in Example 1 ( $Z_1=0.4$ ;  $Z_2=0.89$ ;  $Z_R=1.34$ ). Ninety five percent of the fluoride precipitated was calcium fluoride.

#### EXAMPLE 6

One thousand grams of pond water concentrated to contain 5.0% F and 8.5%  $P_2O_5$  was chilled to 40°F (4°C) and equilibrated with 52.7 grams of a commercial limestone slurried with water (33% solids) ( $Z_1=0.38$ ). After 5 minutes of agitation an additional 131.7 grams of limestone were added and agitation continued for five more minutes ( $Z_2=0.95$ ;  $Z_R=1.33$ ). An 80% fluoride recovery as calcium fluoride solide was realized.

#### EXAMPLE 7

A pond water containing 1% F as a 1:1 mole ratio of HF and  $H_2SiF_6$  and 1%  $P_2O_5$  was treated with a ground limestone slurry (10.5 parts  $CaCO_3$  per 1000 parts pond water by weight). The resulting solution was agitated for 5 minutes ( $Z_1=0.38$ ). About 20% of the fluoride precipitated at this time. Twenty-one grams of additional slurried limestone were added to the solution ( $Z_2=0.76$ ;  $Z_R=1.19$ ); and after 40 minutes of equilibration, the solids were flocculated, settled and separated. The calcium fluoride solids were dried at 105°C and contained about 30% F and about 12%  $P_2O_5$ .

#### EXAMPLE 8

Pond water containing 0.45% F and 0.77%  $P_2O_5$  was agitated and equilibrated with a 35% solids slurry of commercial limestone, in an amount corresponding to 40% of the stoichiometric quantity required for total fluoride precipitation, at room temperature for 5 minutes ( $Z_1=0.40$ ). An additional 70% limestone stoichiometry was added; and at 20 minutes of total reaction time ( $Z_2=0.7$ ;  $Z_R=1.33$ ), 0.12 equivalents of aqueous  $NH_3$  were added per equivalent of initial fluoride and agitation continued for an additional 30 minutes. The resulting mixture was separated into a solid cake and filtrate. The soluble fluoride concentration in the filtrate was 0.56% F. This amounts to a 87% fluoride conversion to calcium fluoride, more than would be anticipated from the amount of calcium added ( $Z_1+Z_2=82\%$   $Z_R$ ). The addition of ammonia apparently made some of the in situ calcium available for reaction with the fluorine.

#### EXAMPLE 9

One thousand grams of Example 1 pond water, at room temperature, was equilibrated with 1.25 equivalents of a 35% solids slurry

of commercial limestone in two steps per equivalent of fluoride ( $Z_1=0.4$ ;  $Z_2=0.85$ ;  $Z_R=1.36$ ). After 19 minutes of reaction, the aqueous phase contained 0.16% F. At this time, 0.069 equivalents of aqueous ammonia per equivalent of initial fluoride were introduced into the reaction mixture. The aqueous phase contained 0.14% F after ten minutes of reaction time. Subsequently, an additional 0.17 equivalents of ammonia per fluoride equivalent were added to the reaction mixture, and after 60 minutes of reaction time, the fluoride concentration in the filtrate was 0.0049%. A 99.4% recovery of fluoride as calcium fluoride was realised. This shows that most of the fluorine in pond water containing a very low F concentration can be recovered as calcium fluoride without excessive  $CaCO_3$  usage.

#### EXAMPLE 10

One hundred grams of dry, raw calcium fluoride solids such as produced in the preceding examples and containing 25.3% F, 14.9%  $P_2O_5$ , 2.11%  $Al_2O_3$ , 52.6%  $CaO$ , 0.44%  $MgO$ , 1.30%  $Fe_2O_3$  and 3.48%  $CO_2$  was slurried with 100 grams of water in a Teflon beaker. To this slurry were added 125 grams of 38.3%  $HNO_3$  which corresponded to 0.955 equivalents of  $HNO_3$  per contained equivalent of  $P_2O_5$  (equivalent weight taken as 23.66) plus 1.00 equivalent of  $HNO_3$  per equivalent of containing  $CO_2$ . The resulting slurry was agitated at room temperature for about 15 minutes and filtered. The collected solids were further washed with three 500 gram portions of water. The leached calcium fluoride solids after drying at 105°C contained 36.8% F and 6.04%  $P_2O_5$ . The acid washing and subsequent water washes removed 71.4 and 8.2% of the initially contained phosphorus and fluorine respectively. The quantity of phosphorus not leached from the raw calcium fluoride was in correlation with the quantities of metallics such as iron, aluminium and magnesium which were not removed.

The acid washing can also be conducted with other mineral acids, such as hydrochloric acid and sulphuric acid, with similar results.

#### EXAMPLE 11

The same calcium fluoride solids that were treated in Example 10 were leached at room temperature with 9.8% aqueous  $H_2SO_4$  using the same procedure as described in Example 10. However, 76.6 and 8.7 percent of the phosphorus and fluorine were leached from the raw calcium fluoride. The washed calcium fluoride solids when dried at 105—110°C contained 22.4% F, 3.3%  $P_2O_5$  and 27.2%  $SO_3$  resulting in the removal of 12% of the F and 78% of the  $P_2O_5$ .



**EXAMPLE 12 (Comparative)**

5 The same dry, raw calcium fluoride solids as was used in Example 10 were slurried to 50% solids with water. The calcium fluoride solids were leached with 60.4% aqueous  $\text{H}_2\text{SO}_4$  such that there existed 1.00 and 1.26 equivalents of sulphuric acid per contained equivalent of  $\text{CO}_2$  and  $\text{P}_2\text{O}_5$  respectively. The temperature ranged from 150 to 200°F (65 to 93°C). After filtration and subsequent water washing, the dry washed calcium fluoride contained 20.6% and 2.11%  $\text{P}_2\text{O}_5$ . About 87.6 and 12.4 percent of the phosphorus and fluorine were contained in the combined leach and wash solutions respectively. At this temperature, approximately 6.2% of the initial fluorine was volatilized from the system.

**EXAMPLE 13**

20 When the same dry, raw calcium fluoride solids as were used in Example 10 were slurried to 50% (w/w) with water, cooled to 4°C and leached with aqueous 4%  $\text{H}_2\text{SO}_4$  at this temperature, no loss in phosphorus leach efficiency was observed.

**EXAMPLE 14**

25 A solution was prepared by combining the separated limestone treated pond water, such as was produced in Example 1, and the acid leach and water wash mixture, such as were produced in Example 11. The solution contained 0.22% F, 1.09%  $\text{P}_2\text{O}_5$ , 0.4%  $\text{SiO}_2$ , and other soluble impurities. To 300 grams of this solution were added 1.44 grams of pure calcium oxide slurried with water. The resulting mixture was agitated for about 20 minutes at room temperature to yield calcium fluoride solids which were removed by filtration. The filtrate had a pH of 3.4 and contained 220 ppm F and 9170 ppm  $\text{P}_2\text{O}_5$ . The weight ratio of P/F in the aqueous phase was increased from 2.16 to 18.2 after the addition of the lime.

**EXAMPLE 15**

45 To 300 grams of the same initial solutions as was used in Example 14 were added 0.72 gram of pure calcium oxide slurried with water and 1.28 grams of a 24.2%  $\text{NH}_3$  solution at room temperature. The resulting solution was equilibrated for 20 minutes to a pH of 3.3 to yield calcium fluoride solids which were removed by filtration. The filtrate contained about 32.2 ppm F and 9200 ppm  $\text{P}_2\text{O}_5$ . In the presence of ammonia, less lime was required to obtain a weight ratio of P/F of about 122 than was required in Example 15 to obtain a P/F weight ratio of 18.2.

**EXAMPLE 16**

60 Pond water was enriched with ammonia to contain about 0.08%  $\text{NH}_3$  and treated with a slurry of commercial limestone in two steps as described in Example 1. After separation

of the calcium fluoride solids, the defluorinated waste water was combined with acid leach and wash solutions to render a composite solution having a pH of 2.0 and containing 0.112% F, 1.10%  $\text{P}_2\text{O}_5$ , 0.28%  $\text{SiO}_2$  plus other values. To 900 grams of this final composite solution at room temperature were added 2.94 grams of a commercial lime; assessed at 85% active CaO, and the resulting mixture was agitated for 35 minutes to a final pH of 3.5 to 3.6. The solid material formed was flocculated, settled and separated from the aqueous phase which contained 0.0027% F and 0.905%  $\text{P}_2\text{O}_5$  and a weight ratio of P/F of 146. The solid material precipitated after drying at 105–110°C contained 19.5% F, 23.3%  $\text{P}_2\text{O}_5$ , 44.0% CaO, 1.47%  $\text{SiO}_2$ , 0.21%  $\text{NH}_3$  plus other minor values. This solid material is suitable for acid leaching and washing to obtain a further quantity of calcium fluoride.

**EXAMPLE 17**

To 200 grams of a composite solution similar to that used in Example 16 but containing 4.69%  $\text{P}_2\text{O}_5$  and 0.87% F were added 5.13 grams of pure lime slurried with water and 6.47 grams of a 29.0%  $\text{NH}_3$  solution. This mixture was agitated for about 15 minutes to a pH of 4.0 while the temperature decreased from 180°F to about 150°F (82 to 65°C). The filtrate contained 3.18%  $\text{P}_2\text{O}_5$  and 0.0078% F yielding a P/F weight ratio of 178.

**EXAMPLE 18**

The procedure of Example 17 was conducted at 40°F (4°C) with no adverse effects on the resulting P/F ratio in the final filtrate.

**EXAMPLE 19**

646.4 grams of the final aqueous solution, having a P/F weight ratio of 146, produced in Example 16 were treated with 3.89 grams of a commercial lime slurried with water. The resulting mixture was agitated at room temperature for 15 minutes. The pH increased from 3.6 to 6.7. The solid precipitate was recovered by decantation and filtration, dried at 105 to 110°C, and found to contain 0.08% F, 39.2%  $\text{P}_2\text{O}_5$ , 31.9% CaO, 2.4%  $\text{SiO}_2$ , 21.8% weight loss at 800°C, plus other minor values. This solid having the stoichiometry of dicalcium phosphate,  $\text{CaHPO}_4$ , contained a P/F weight ratio of 214. This same solid contained 44.7%  $\text{P}_2\text{O}_5$  when dried at 164°C.

**EXAMPLE 20**

To a solution containing 2.95 ppm F and 1.23%  $\text{P}_2\text{O}_5$  was added slurried commercial lime to a final pH of about 8.5. The mixture was agitated at room temperature for 90 minutes and the solids were recovered by filtration and were dried at 105 to 110°C.

The solid material analyzed 0.14% F, 39.7%  $P_2O_5$ , 37.4% CaO, 6.3%  $SiO_2$  (P/F=124).

#### EXAMPLE 21

5 An initial solution similar to that used in Example 20 was treated with commercial lime to a pH of 6.2. The solids dried at 105 to 110°C contained 0.12% F, 40.6%  $P_2O_5$  and 30.7% CaO (P/F=148).

#### EXAMPLE 22

10 A reaction similar to that of Example 21 was conducted at 180°F (82°C). No adverse effects on the final product were observed.

#### EXAMPLE 23

15 A reaction similar to that of Example 21 but performed at 40°F (4°C) showed no adverse effects on the solid material.

#### EXAMPLE 24

20 A solution containing 0.0010% F, 0.10%  $P_2O_5$  and 0.3%  $SiO_2$  at a pH of 7.0 was treated with slurried lime to a pH of 9.0 and agitated to 30 minutes. The water decanted from the settled solution contained minute amounts of F,  $P_2O_5$  and  $SiO_2$ .

#### EXAMPLE 25

25 A pond water containing 0.85% F, 1.49%  $P_2O_5$ , plus other impurities was heated to 203°F (95°C) and was then equilibrated with a total of 1.35 equivalents of commercial limestone per contained equivalent of fluoride in two stages as described in Example 1. In the first stage  $Z_1$  calcium equivalents added equalled 0.4 and the  $Z_2$  calcium equivalents equalled 0.95 in the second stage ( $Z_R=1.34$ ). After 20 minutes of reaction time and subsequent separation of the solid material, the recovered solids at 105°C drying, contained 25.6% F, 14.2%  $P_2O_5$ , 50.3% CaO, 1.8%  $SiO_2$ , plus other impurities and hydrated water. This material was of the same nature as found in Example 1 and shows that the precipitation of fluoride is not extremely dependent on temperature. The filtrate obtained was heated to 203°F (95°C) and was combined with slurried commercial lime to obtain a pH of 3.6, when calcium fluoride solids formed. The solids were separated from the liquid by decantation and filtration and analyzed 9.0% F, 31.7%  $P_2O_5$ , 48.6% CaO, 1.4%  $SiO_2$ , plus other impurities when dried at 105°C. The aqueous phase, which had a  $P_2O_5$ /F weight ratio of 333, from this reaction was heated to 194°F (90°C) and equilibrated to pH 7.2 with slurried commercial lime to form "dical" solids. After about 15 minutes of reaction, the "dical" solids were separated by decantation and filtration and were dried at 105°C. This material contained 0.21% F, 21.5%  $P_2O_5$ , 46.4% CaO, 9.1%  $SiO_2$ , plus other impurities and is suitable for granulation with phosphoric acid.

#### EXAMPLE 26

Pond water containing 1.01% F and 1.84%  $P_2O_5$  was first treated with 560 ppm of  $NH_3$  and then reacted with a 35% solids slurry of commercial limestone, the solid material isolated and the filtrate combined with sulphuric acid wash solutions such as prepared in Example 12. In the first stage,  $Z_1=0.38$  calcium equivalents were added and in the second stage,  $Z_2=0.81$  calcium equivalents were added ( $Z_R=1.35$ ). This final mixture containing 0.27% F and 1.70%  $P_2O_5$  was raised to a pH 3.5 to 3.6 with a 20% solids slurry of commercial lime and held at this pH for 20 minutes to render a P/F weight ratio of 153 in the aqueous phase after recovery of the solids. This liquid phase was further equilibrated with commercial lime to a pH of 10.0 for about 15 minutes. The recovered solids contained dicalcium phosphate and nearly all of the silica which would otherwise remain in solution at pH values of about 7.0 to 7.5 or less.

#### EXAMPLE 27 (Comparative)

A pond water containing 0.3% F and 0.05%  $P_2O_5$  was treated with one equivalent of calcium as a 33% solids slurry of limestone per equivalent of contained fluoride with the mixture agitated for fifteen minutes ( $Z_1=1.00$ ). An additional 0.01 equivalents of calcium per equivalent of contained fluoride were further added ( $Z_2=0.01$ ;  $Z_R=1.03$ ) and equilibrated by agitation for forty-five additional minutes. The calcium fluoride precipitate contained 40% F and 1%  $P_2O_5$ .

#### EXAMPLE 28 (Comparative)

A pond water containing 0.3% F and 2.0%  $P_2O_5$  was treated with a 33% solids slurry of limestone such that 1.1 equivalents of calcium were added per equivalent of contained fluoride ( $Z_1=1.1$ ). The mixture was equilibrated by agitation for five minutes after which time 1.19 equivalents of calcium per equivalent of contained fluoride were added ( $Z_2=1.19$ ;  $Z_R=2.29$ ), and the solution equilibrated for an additional thirty minutes. The precipitated calcium fluoride contained 14% F and 28%  $P_2O_5$ .

#### EXAMPLE 29

One thousand grams of pond water containing 0.7% F and 1.3%  $P_2O_5$  along with varied levels of other substances normally found in pond water was treated at 95°F (35°C) with 7.76 grams of 95% effective limestone slurried as a 40% mixture with water and agitated for five minutes ( $Z_1=0.4$ ). To this mixture was added an additional 18.63 grams of limestone as in the previous manner and the agitation was continued for an additional thirty minutes ( $Z_2=0.96$ ;  $Z_R=1.36$ ). A raw calcium fluoride slurry containing 40% solids was collected by filtration



of the reaction mixture and contained 23.80 grams of solids that, dried at 105°C, were found to contain 25.0% F, 15.0% P<sub>2</sub>O<sub>5</sub> and 2.0% CO<sub>2</sub>. The filtrate or treated pond water contained 1.59 grams of fluorine and analysed 0.12% F and 1.11% P<sub>2</sub>O<sub>5</sub>. A sulphuric acid wash was applied to the raw calcium fluoride slurry, the slurry being combined with 7.49 grams of sulphuric acid as ten percent aqueous solution and agitated for fifteen minutes at 95°F (35°C). Subsequent to filtration of the solids the filter cake was washed with two 119 gram portions of water. The 23.80 grams of dry calcium fluoride contained 22.7% F and 3.74% P<sub>2</sub>O<sub>5</sub> with the diluent being primarily calcium sulphate. The combined acid and water wash filtrates were combined with the treated pond water to give 951.13 grams of a solution containing 0.17% F and 1.82% P<sub>2</sub>O<sub>5</sub>. This solution was made to contain 500 ppm NH<sub>3</sub> by the addition of a 25% NH<sub>3</sub> aqueous solution. Further treatment at 95°F (35°C) with 4.10 grams of 95% effective lime as a 20% water slurry brought the solution to a pH of from 3.7 to 3.8 and with 15 minutes of agitation resulted in the precipitation of a second calcium fluoride solid having a dry-base analysis of 20.0% F and 20.0% P<sub>2</sub>O<sub>5</sub> and amounting to 7.77 grams. This material in slurry form was taken back to the sulphuric acid leach stage and recycled through the system. The resulting filtrate contained 0.0031% F, 1.11% P<sub>2</sub>O<sub>5</sub> and amounted to 954.12 grams. A further lime treatment comprised the addition of 7.48 grams of lime as in the previous manner in order that a pH of 6.9 to 7.1 was maintained at 95°F (35°C) with fifteen minutes of agitation. The resulting 25.43 grams of dry calcium phosphate contained 0.12% F and 39.5% P<sub>2</sub>O<sub>5</sub>, a P/F weight ratio of 144, and was suitable for granulation to produce a feed grade material. The filtrate contained 0.0011% F, 0.056% P<sub>2</sub>O<sub>5</sub> and all of the soluble silica initially present in the pond water. By this scheme of pond water treatment, 99.6% of the fluorine was converted into a synthetic calcium fluoride and 77.1% of the phosphate was transformed into a material which conforms to the P/F of 100 ratio necessary for a feed grade phosphate.

#### WHAT WE CLAIM IS:—

1. A method of treating waste water resulting from the production of wet process phosphoric acid and containing fluorine and P<sub>2</sub>O<sub>5</sub> values, comprising: in a first stage, agitating said waste water with an amount of calcium carbonate to provide between 0.3 and 0.8 equivalents of calcium per equivalent of fluorine (F) values in the water; thereafter, in a second stage, agitating the calcium carbonate-treated waste water with additional calcium carbonate in an amount to form calcium fluoride solids, and such that the total calcium

carbonate addition in the two stages provides not less than 0.8 equivalents of calcium per equivalent of F values in the waste water; and separating the solids from the aqueous phase following said second stage.

2. A method according to Claim 1, including the additional step of treating the waste water with ammonia to establish an ammonia concentration of from 10 to about 5000 ppm by weight in said water.

3. A method according to Claim 2, wherein the ammonia addition is such as to establish an ammonia concentration within the range 600 to 800 ppm by weight in the water.

4. A method according to Claim 2 or 3, wherein the ammonia is added to the calcium carbonate-treated waste water effluent of said first stage.

5. A method according to any one of Claims 1 to 4, wherein about 0.4 equivalents of calcium per equivalent of fluorine in the waste water are added thereto in said first stage.

6. A method according to any one of Claims 1 to 5, wherein the calcium carbonate addition in the second stage is such as to provide a total calcium addition in the range 1 to 2 equivalents of calcium per fluorine equivalent.

7. A method according to any one of Claims 1 to 6, wherein the said solids separated from the second stage effluent are first washed with an aqueous solution of a mineral acid to remove acid soluble values and thereafter are washed with water to remove mineral acid and aqueous soluble values, thereby to produce solids enriched in calcium fluoride.

8. A method according to Claim 7, wherein the said solids values are washed with an amount of mineral acid about equivalent to the total of the P<sub>2</sub>O<sub>5</sub> values and CO<sub>2</sub> values contained in the solids.

9. A method according to Claim 7 or 8, wherein the treated waste water effluent of said second stage, after separation of the said solids, is combined with the aqueous mineral acid washings and the water washings from said solids to form an aqueous mixture, and such aqueous mixture is agitated with calcium oxide in an amount sufficient to raise the pH of the aqueous mixture to a value ranging from 3 to 4, thereby to convert a substantial portion of the remaining fluorine values in the aqueous mixture to insoluble calcium fluoride solids.

10. A method according to Claim 9, wherein the calcium fluoride solids are separated from the treated aqueous mixture to yield a second crop of calcium fluoride solids.

11. A method according to Claim 10, wherein the second crop of calcium fluoride solids is washed with an aqueous mineral acid to remove the acid soluble values therefrom and then washed with water to remove acid and water soluble values therefrom to produce solids enriched in calcium fluoride.

12. A method according to Claim 10, wherein the second crop of calcium fluoride solids is combined with the solids separated from the second stage effluent prior to the acid washing of said separated solids.

13. A method according to Claim 10, 11 or 12, wherein the treated aqueous mixture, after separation of the said calcium fluoride solids, is treated with additional calcium oxide to raise the pH of the aqueous mixture to a value ranging from 5 to 8 to form insoluble dicalcium phosphate solids.

14. A method according to Claim 13, wherein the insoluble dicalcium phosphate solids are separated from the calcium oxide-treated aqueous mixture.

15. A method according to Claim 14, wherein the treated aqueous mixture, after said separation of the said dicalcium phosphate solids, is further treated with calcium oxide to raise the pH of the aqueous mixture to a value ranging from 8 to 11 to remove a substantial portion of the soluble mineral values from the aqueous phase by the formation of insoluble mineral solids.

16. A method according to Claim 15, wherein the insoluble mineral solids are separated from the treated aqueous mixture, yield-

ing an aqueous phase substantially free of fluorine,  $P_2O_5$ , calcium and silicon dioxide values.

17. A method according to any preceding Claim, wherein in each of said first and second stages the calcium carbonate is in the form of an aqueous slurry containing 5% to 50% by weight calcium carbonate.

18. A method of treating the waste water of a wet process phosphoric acid plant, according to Claim 1 and substantially as described with reference to the accompanying drawings.

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